

Bimetallic Ru/Mo Catalyst Particles for HDN of Tetrahydroquinoline

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ABSTRACT:

Ethanol solutions of the heteropolyanion $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$, (Mo-HPA) mixed with RuCl_3 were decomposed, at 180°C in the presence of CS_2 and H_2 to form small multimetallic catalyst particles. Previous efforts have demonstrated the synergistic effect of these catalyst systems for Quinoline hydrogenation to THQ and alkylation of THQ by ethanol. The current study extends these efforts to the HDN of THQ in hexadecane.

INTRODUCTION

We have previously shown that alumina supported RuMo and RuCoMo bi- and trimetallic catalysts provide catalytic activities and product selectivities during quinoline (Q) and tetrahydroquinoline (THQ) hydrodenitrogenation (HDN) that are not normally observed with alumina supported, $\text{M}'\text{Mo}$ ($\text{M}' = \text{Co}, \text{Ni}$) or single metal Mo or Ru catalysts.¹⁻⁷ The RuMo combination of metals appears to offer synergistic behavior during Q and THQ HDN. In particular, the catalysts are sulfur tolerant, even showing enhanced activities in the presence of sulfur compounds. Their activities are 5 to 10 times higher than corresponding $\text{M}'\text{Mo}$ catalysts for similar weight loadings on identical supports. Moreover, their selectivity towards the formation of propylbenzene vs. propylcyclohexane during Q or THQ HDN is much higher (1:3 product ratios at temperatures of 350°C and H_2 pressures of 400-600 psig at RT).

In an effort to completely delineate this synergistic behavior, we have examined the catalytic activity of RuMo catalysts with Q and THQ under a variety of conditions. Furthermore, we have examined the feasibility of preparing these heterogeneous bimetallic catalysts directly from soluble precursors based on ethanolic solutions of molybdenum heteropolyanion, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (Mo-HPA) and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Ru-Cl).

We find that 1:9 Ru:Mo atomic ratio solutions consisting of 1.0 ml (5.7×10^{-3} M, 5.7×10^{-3} mmol) of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ in EtOH with 4.0 ml of 1.1×10^{-3} M in Mo-HPA (4.38×10^{-3} mmol) in EtOH, when heated with 5.0 ml (42 mmol) Q or THQ and 50 μl of CS_2 for 3 h at 175-200°C decompose uniformly to give 0.3-1.5 μm dia. RuMo catalyst particles (surface areas typically of 5-9 m^2/g).^{6,7} These bimetallic particles appear to be more catalytically active for Q hydrogenation to THQ than similar particles generated either from Mo-HPA or Ru-Cl under identical conditions.⁷ Furthermore, efforts to promote HDN of

THQ at somewhat higher temperatures in EtOH solutions leads to the N-ethylation of THQ rather than HDN.⁶ Again, the RuMo catalyst is much more effective for N-ethylation than either of the metals alone. N-ethylation was also observed when THQ HDN was attempted in acetonitrile solutions of RuMo. We have now determined that it is possible to conduct THQ HDN to the exclusion of extraneous reactions through the use of hexadecane as solvent. We describe here preliminary efforts to study this reaction.

EXPERIMENTAL

HDN catalysis studies were conducted using hexadecane as solvent and using 1:9 RuMo catalyst particles generated under conditions identical to the Q hydrogenation reactions, at 175°C, but in the absence of Q.⁷ Particle surface areas were 5-6 m²/g. Studies were done with two 250 mg batches of catalyst which were mixed to obtain a uniform catalyst.

Product analyses for all the kinetic studies were performed on a temperature programmed Hewlett-Packard 5890A reporting GC equipped with FID using a 12 m x 0.53 mm x 2.65 μ m capillary column packed with 100 % dimethyl polysiloxane gum. The column heating schedule was initiated with a hold at 35°C (2 min) followed by ramping at 7°C/min to 250°C. The eluting gas mixture was H₂/He.

GC-MS studies were performed using an HP 5890 Series II GC, an HP 5970 mass spectrometer, and the HP 5940 MS Chemstation. The capillary column used for product separation was a 12 m x 0.12 mm x 0.33 μ m film thickness HP-5 (crosslinked 5% phenyl methyl silicone) capillary column. The temperature for the analysis was held at 50°C for 5 min, then ramped at 4°C/min to 275°C. The eluting gas used was H₂/He.

THQ HDN Kinetic Runs

Typically, 18-20 mg of catalyst are added to a solution of 5.0 ml (42.3 mmol) of THQ mixed with 5.0 ml of hexadecane and 50 μ l of decane as internal standard in a quartz lined, Parr General Purpose Bomb reactor with a 34 ml internal volume. The reaction solution is then pressurized to 400 psig with N₂ at RT and depressurized. The process is repeated and then 400 psig with H₂ at RT is added and the reaction is heated, with magnetic stirring, to the desired temperature, e.g 370°C for the studies shown below. At the appropriate times (typically 3, 6, 9, 12 and 15 h) the reactor is cooled in flowing water, depressurized and a sample is taken for GC analysis. The reactions are run to less than 5% conversion so that the initial rates of product formation correspond essentially to zero order in reactant concentration.

RESULTS AND DISCUSSION

Figure 1 shows the standard reaction network for Q HDN.⁸ Propylcyclohexene may arise both from hydrogenation of propylaniline and from deamination of aminopropylcyclohexane, presumed to be an intermediate in DHQ HDN. Propylaniline and DHQ are presumed to derive directly from catalytic reactions of THQ, and propylbenzene and propylcyclohexane are presumed to arise from the catalytic reactions of propylaniline and DHQ respectively; although propylcyclohexane could also derive from propylbenzene.

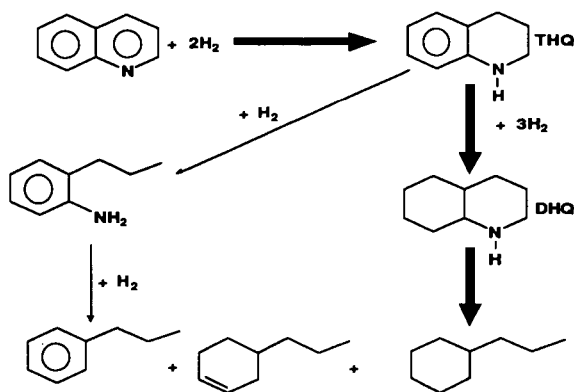


Figure 1. Quinoline HDN Reaction Network

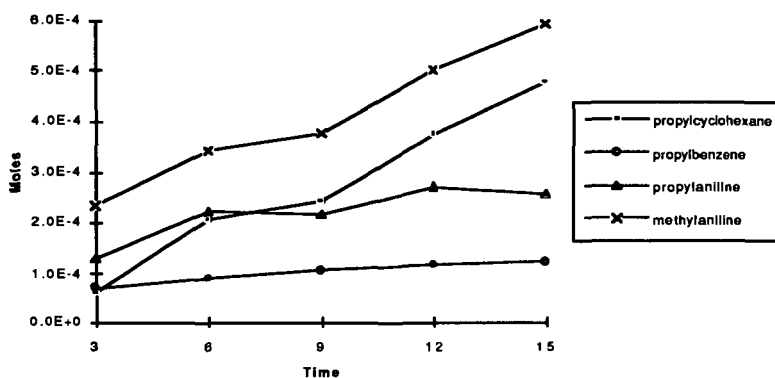
Figure 2 shows a plot of the major bond cleavage products observed at 370°C during RuMo catalyzed HDN of THQ, as a function of time. In Figure 2, the quantities of propylaniline initially produced are not significantly higher than the propylbenzene. Furthermore, [propylcyclohexane] increases significantly with time whereas [propylbenzene] does not. Given that the amount of products produced during the course of the reaction all fall in the 0.1 to 0.8 mmol range and the starting amount of THQ is on the order of 42 mmol, the percent conversion of THQ is of the order of 1%. Normally, the sequential formation of products, as depicted in Figure 1, should not lead to the formation of significant amounts of secondary products such as propylbenzene or propylcyclohexane at conversions of 1%. Thus, these results are rather surprising.

We offer two explanations for these observations, the first is that the catalyst particles are highly porous and that much of the catalysis occurs in the particles' interiors. In this case, the actual concentration of reactants at the catalyst surface would be much higher than it is in solution and secondary products might be expected to escape from the porous body at about the same rate as primary products. Hence the relative concentrations of the two types of products seen by GC would be representative of the mixture in the particle rather than in solution.

The second possibility is that once THQ is bound to the active catalytic site in these unsupported catalyst particles, it remains bound for sufficient periods of time to undergo more than one type of catalytic reaction. This would mean that the site would have a higher affinity for the reaction products and would be able to perform several different types of catalytic operations.

At this point, it is not possible to distinguish between the two possibilities; however, the surface

areas of the particles and the SEM micrographs^{6,7} bely the possibility of a very porous catalyst particle. But the conversions are sufficiently low that it may be that some of this type of porosity exists and is responsible for most of the catalytic activity. Further studies will be required to differentiate between these, or other, possible explanations.



Finally, the appearance of significant quantities of methylaniline, a product of C-C rather than C-N bond hydrogenolysis suggests that there are Ru rich regions on the catalyst particles as this product is more typical of bulk Ru catalyzed HDN of THQ.⁵

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